

CERTAIN CHEMICAL CHARACTERISTICS OF
EDIBLE FATS AND OILS

by

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INTRODUCTION

An ever increasing number of commercial fats and oils for use in cookery have appeared on the market in recent years but there is apparently a lack of information concerning certain chemical characteristics of these fats and oils. Individual manufacturers have laboratories in which chemical tests are made of the products of that particular company. These findings are published largely as a means of sales promotion.

The publication of the little work that has been done in non-commercial laboratories, with few exceptions, dates back to 1915; improved methods of manufacturing fats and oils would tend to make these findings invalid. Deep-fat frying is becoming an even more popular method of cooking various foods as the public is becoming better informed of improved procedures in the actual cooking of fried foods and of facts concerning fats and oils in the diet. To use a fat most economically involves accurate knowledge regarding the point at which the fat decomposes. Information regarding chemical characteristics of fats and oils is therefore needed by institutional managers, foods instructors, research workers and homemakers.

The purpose of this investigation was to study certain chemical characteristics of twenty-seven fats and oils which might be related to the suitability of the fat or oil for deep-fat frying.

METHOD

This study was divided into two parts. The first part was the determination of the smoking point of fats and oils using both a visual method and a chemical method. The second part of the study was made to obtain the percentage of free fatty acids, as oleic acid, in these fats and oils using (1) fresh samples and (2) samples after heating for 2-, 6-, 12-, and 20-hour periods.

Smoking Point, the Visual Method

The method used in this study was a modification of the methods used by Blunt and Feeney (1915) and the one adopted by the American Oil Chemists' Society (1934).

A small electric heater with a rheostat control and a removable refractory top plate made of claystone with a three-inch circular opening beveled on each side was used throughout all of the experiments. The rheostat permitted the rise in the temperature of the fat to be regulated as desired. In order to afford more circulation of air around the sample than would have been possible had the evaporating dish been placed directly on the top plate, a metal grate was placed over the plate. This raised the evaporating dish and frying pan to a plane level with the top of

the heater and aided in the temperature control. Even though the heater was equipped with a rheostat, when the dishes were placed directly on the plate the fat tended to heat too rapidly.

A preliminary test was made to find the approximate smoking point of each fat. After such a test, a 50-gram sample of fat was heated in a four and one-half inch silica evaporating dish at a fairly rapid rate to within about 75°C . of the smoking point. The heat was then decreased by means of the rheostat control on the electric heater. An Eastman timer was started in order that the rise in temperature of the fat could be noted and the rheostat was regulated so the rise was not more than 5°C . in 10 minutes. A Centigrade thermometer graduated in degrees from 0° to 250° was used for determining the decomposition point. The temperature at which the sample gave off a thin, bluish smoke continuously was regarded as the smoking point. The smoke was more readily observed by using a black background. After the temperature had been read and recorded, the sample was removed from the stove, cooled and then reheated. This process was repeated twice. In this manner three readings were taken on three fresh samples of each fat and oil, each result being an average of nine determinations.

After these experiments were completed, a six-inch metal frying pan was substituted for the silica evaporating dish and the experiments repeated. This was done in order that any difference in the smoking points due to using a container with a greater surface area could be noted. In this group of experi-

ments only one sample of each fat was used and three determinations were made on each fat sample.

Smoking Point, the Chemical Method

Acrolein, the decomposition product obtained when fats and oils have been heated to the smoking point, is an aldehyde. In order to supplement the data obtained by the visual method described above, the method of Sprague (1919) which is the fuchsin test for aldehydes was used. This test is dependent upon the color change of the reagent, fuchsin bisulphite, from colorless to a distinct purple in the presence of aldehydes. The fuchsin bisulphite, or Schiff's reagent, was prepared by dissolving one gram of para rosaniline hydrochloride in one liter of distilled water. This was filtered from any residue. Another liter of distilled water was saturated with sulphur dioxide and mixed thoroughly with the filtered rosaniline hydrochloride solution.

Throughout these experiments an electric heater (A) with a rheostat control was used. A 50 cc. sample of melted fat was heated in a four and one-half inch silica evaporating dish (B) covered closely by an enamel funnel (C) (Plate I). The large end of the funnel measured five inches in diameter, the small end two inches. The one and one-half inch stem of the funnel was fitted with a two-hole rubber stopper (D). This stopper was fitted with a thermometer (E) reading in degrees from 0° to 250°C., and with an eight-inch glass tube (F) with a right-angle bend at

the mid-point. Connected to the glass tube (F) was a rubber tube (G) 12 inches in length. The other end of the rubber tubing was connected with an eight-inch piece of glass tubing (H) with a right-angle bend at the mid-point. A seven-eighths inch rubber stopper (I) was fitted to the glass tubing (H). This rubber stopper was placed in a U-tube (J) six inches in length which contained 10 cc. of fuchsin bisulphite solution. The U-tube was immersed in a one liter beaker (K) containing ice water. A rubber stopper (L) closed the other side of the U-tube. Inserted in this stopper was an eight-inch glass tube with a right-angle bend at the mid-point (M). An eight-inch piece of rubber tubing (N) was attached to the glass tubing and was directed to a safety bottle (O) used to prevent water from backing up into the apparatus.

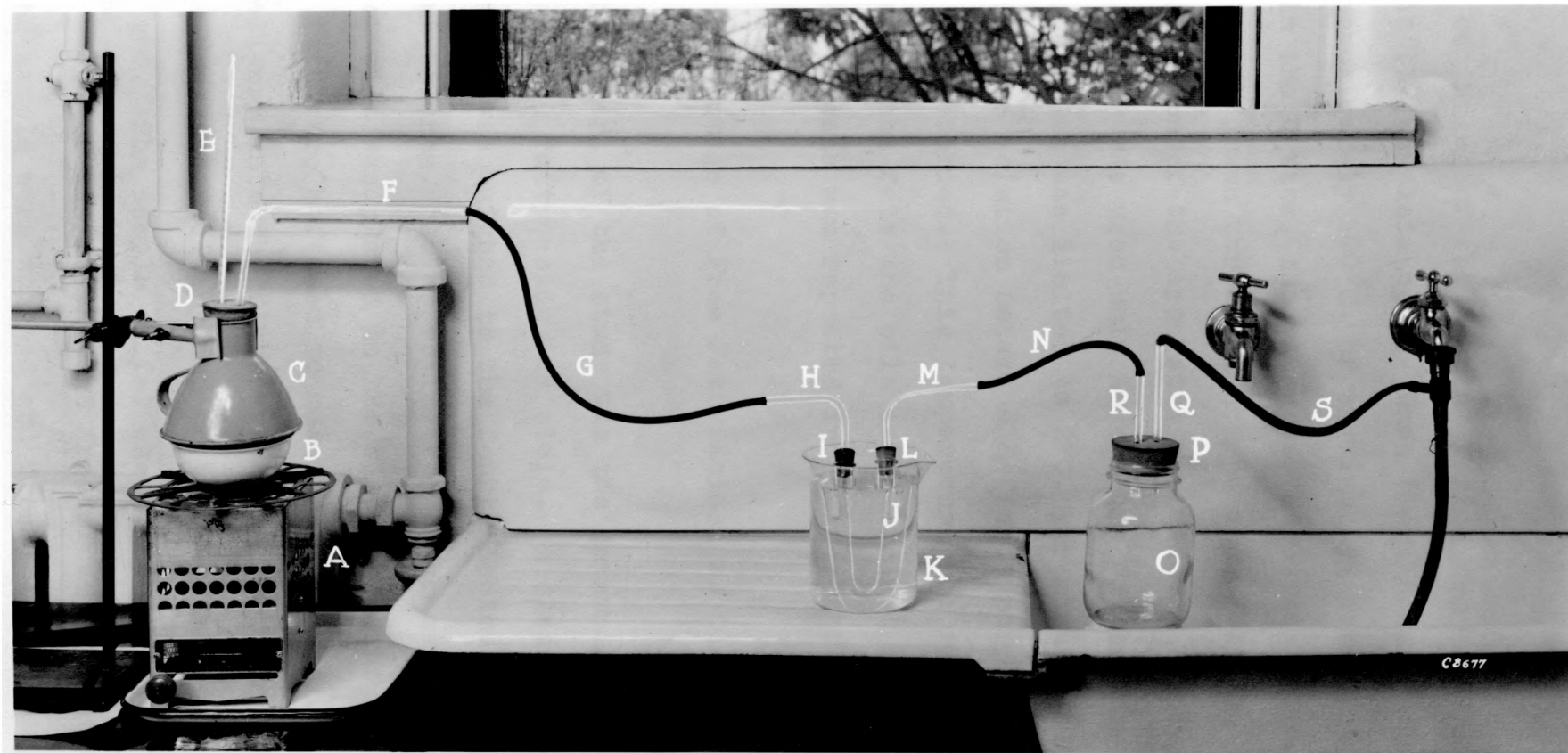
The safety bottle was fitted with a two-hole rubber stopper (P) which measured two and three-fourths inches in diameter. This stopper was fitted with two six-inch pieces of glass tubing (Q and R). One of the glass tubes was connected to the rubber tubing (N), the other to a piece of rubber tubing (S) 12 inches in length, which was fastened to a filter pump. When all connections were made and the filter pump was operating, the air passing over the fat was drawn through the fuchsin bisulphite solution in the U-tube. The flow of water which operated the filter pump was so regulated that the rate was even and the bubbles passed very slowly through the reagent.

EXPLANATION OF PLATE I

Apparatus used for determining the smoking point of the fats and oils using the chemical method.

- | | |
|---|-------------------|
| A. Electric heater | L. Rubber stopper |
| B. Evaporating dish | M. Glass tubing |
| C. Enamel funnel | N. Rubber tubing |
| D. Rubber stopper | O. Safety bottle |
| E. Thermometer | P. Rubber stopper |
| F. Glass tubing | Q. Glass tubing |
| G. Rubber tubing | R. Glass tubing |
| H. Glass tubing | S. Rubber tubing |
| I. Rubber stopper | |
| J. U-tube containing fuchsin bisulphite | |
| K. Liter beaker containing ice water | |

PLATE I



At the beginning of the heating period for each sample the connection at (I) was left open. When the fat sample was heated to within approximately 100°C . of the smoking point, the stopper was placed in the U-tube, the water tap adjusted and any fumes over the fat were drawn through the apparatus. At the same time that the connection of the apparatus was made an Eastman timer was started. This was used only as a means of checking the rise in temperature which was limited to 2°C . per minute. When the fuchsin bisulphite solution became a definite purple color the temperature was recorded. This temperature was regarded as the smoking point of the fats and oils as determined by the chemical method. This process was repeated in duplicate for each fat.

Percentage of Free Fatty Acids, as Oleic

The second part of the study was the determination of the percentage of free fatty acids, as oleic. A clean, dry 300 cc. Erlenmeyer flask was weighed to the fourth decimal place using an analytical balance. An approximate 10-gram sample of the fresh fats or oils was placed in the flask by means of a pipette. The fats were softened to make possible the use of the pipette. Delivery into the flask was hastened by having cut three inches from the delivery end of the pipette and having fire glazed this end. The sample of fat was placed in the flask with care so the sides of the flask were free of any fat droplets. The flask and sample were weighed and from this weight was

deducted the weight of the clean flask. This resulted in the exact weight of the sample. Fifty cc. of 95 per cent ethyl alcohol and several glass beads were added to the fat. The contents of the flask were brought to a boil in a water bath. The flask was placed in a water bath at 60°C . and allowed to cool to that temperature. The sample was titrated with approximately 0.10 N. NaOH using two drops of phenolphthalein as an indicator. The phenolphthalein solution was prepared by dissolving one gram of phenolphthalein in 35 cc. of pure ethyl alcohol and diluting with 65 cc. of distilled water. The NaOH solution used was actually 0.1096 N. Three determinations were made for each sample.

To determine the effect of heating on the free fatty acid content, 300 grams of each fat and oil were placed in clean, white enamel sauce pans. The sauce pans had a diameter of five inches and a depth of three inches. The samples were heated in a gas oven equipped with a three-foot rotating hearth so as to insure uniform temperature. The oven was especially constructed for experimental work and was well insulated so exact temperatures could be maintained. A thermometer was suspended in one of the samples during each period of heating so the temperature was that of the fat rather than that of the oven. The samples were heated for two hours at $193^{\circ}\text{C} \pm 3^{\circ}\text{C}$. As a rule, either 7 or 14 samples were heated at one time depending on convenience for working. Three 10-gram samples of each fat and oil were removed from the enamel pan, were weighed and titrated. The same process was repeated after 6, 12 and 20 hours of heating.

The method given below was used for the calculation of the percentage of free fatty acids, as oleic.

Factor: 1 cc. N/10 alkali is equivalent to 0.0282 gms. oleic acid. This factor is given by Morrow and Sandstrom (1927) and is the one cited in physiological chemistry laboratory manuals.

The normality of the alkali used was 0.1096 N. To determine the factor using this normality the following equation was solved:

$$N/10 : \text{Normality of alkali used} = 0.0282 : x.$$

x = factor for the normality of alkali used.

(Wt. of dry flask + fat) - wt. of flask = wt. of sample of fat.

[0.2 cc. was deducted from the total cc. alkali used for blank determination

total alkali used - 0.2 cc. for blank determination = cc.

alkali to neutralize fatty acids

(total alkali used - 0.2 cc.) \times factor = total gms. acid expressed as oleic]

or

[cc. alkali to neutralize fatty acid \times factor = total gms. acid expressed as oleic]

(gms. oleic acid \div wt. of sample of fat) \times 100 = per cent free fatty acid, as oleic.

Example:

$$\frac{0.1000}{0.1096} = \frac{0.0282}{x}$$

$$0.1 \times = 0.00309$$

$$x = 0.0309$$

∴ 1 cc. 0.1096 N. alkali is equivalent to 0.0309 gms. oleic acid.

Wt. of flask + fat	57.4255 gms.
Wt. of flask	- 46.4509 gms.
Wt. of sample of fat	<u>10.9746 gms.</u>

0.0309 gms. oleic acid equivalent to 1 cc. of 0.1096 N. NaOH
x 0.2 cc. of alkali used
<u>0.00618 gms. oleic acid</u>

$$\frac{0.00618 \text{ total gms. oleic acid}}{10.97460 \text{ gms. in sample of fat}} \times 100 = 0.0562 \text{ per cent free fatty acid, as oleic.}$$

Morrow and Sandstrom (1927) have stated, "the acid number is defined as the number of milligrams of potassium hydroxide, required to neutralize the free fatty acids in one gram of fat, oil or wax." To calculate the acid number of a fat, the percentage of free fatty acids, as oleic, is multiplied by the factor 1.99. This factor is cited by Griffin (1927). The factor 1.99 is derived by the following method:

1 cc. of 0.1 N. KOH equivalent to 0.02823 gms. oleic acid

1 cc. of 0.1 N. KOH equivalent to 5.61 mg. KOH

$$\frac{5.610}{2.823} = 1.99$$

Example:

0.0140 percentage of free fatty acid, as oleic
x 1.99 factor
<u>0.0278 acid number</u>

The following fats and oils were used in this study:

Advance Shortening
Armour's 100 per cent Leaf Lard
Armour's Star Lard
Clix
Cocoanut Oil
Covo
Crisco
Dexo
Flakewhite
Homemade lard
Kneedit
Mazola
M. F. B.
Peanut Oil
Penick Oil (Flufffo)
Puritan Oil
Primex
Primex B and C
Rex Lard
Snowdrift
Soybean Oil
Spry
Sunnyfield
Swift's Silverleaf Bland Lard
Vegetole
Wesson Oil
Wilson's Lard

REVIEW OF LITERATURE

Published results of work in non-commercial laboratories regarding fats and oils date back to years around 1915. Although greatly improved fats and oils are now manufactured but little information regarding the various products has been made available to the consumer.

Blunt and Feeney (1915) whose work with fats and oils is among the first to be recorded found a relationship between the smoking point and the free fatty acid content; i.e., the higher

the smoking point the lower the percentage of free fatty acids. These workers found that the surface exposed greatly affected the smoking point of a fat. A sample of Crisco in an evaporating dish, the diameter of the fat surface being 3.25 inches, had a smoking temperature of 231°C . When using a saucepan, the diameter of the fat surface being seven inches, the smoking point was 220°C . When an iron kettle was used with a diameter of fat surface of 10.25 inches, the smoking point was 206°C . There were corresponding temperatures for the bulk lard used in this series of experiments, those being 194°C ., 183°C . and 169°C . respectively. A simple, visual method for determining the smoking point of fats was used by these workers as it was thought to be most nearly like actual cooking conditions. It was also found by these workers that in the advertisement of one fat, the smoking temperature was the same as that resulting from the three and three-fourths inch evaporating dish used in the experiments, but that temperature was 25°C . above that obtained when a large kettle was used.

A method was suggested by McCoy (1926) in which a 100 cc. round-bottom Pyrex flask was used for the fat sample. A thermometer was suspended in the fat. The first few wisps of smoke collected in the neck of the flask; thus the smoking temperature recorded was lower than the actual decomposition point.

This method not being entirely accurate was discontinued although a modification of this method was adopted by the American Oil Chemists' Society (1934). A three-sided cabinet was

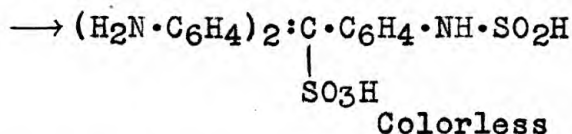
used into which the apparatus was placed. A beam of light from a 100-watt daylight bulb encased in a tin cylinder was directed across the center of a Cleveland Open Cup Tester. The cup was filled so the top of the meniscus was exactly at the filling line of the cup. The cup measured two and one-half inches in diameter. A single piece of asbestos was placed on the ring-stand under the cup in order to do away with waves of heat. The flame used was that of an ordinary Bunsen burner. The oil was heated to within approximately 75°F . of the smoking temperature. The flame was then regulated so there was a rise in temperature of not less than 9 or more than 11 degrees F. per minute. The smoking point was taken as the temperature at which the sample gave off a thin, bluish smoke continuously.

A chemical test for determining the decomposition point of edible fats based upon the fuchsin test for aldehydes was used by Sprague (1919). The results in this work were in accordance with those of Blunt and Feeney; i.e., the greater the surface area exposed the lower the smoking point. The smoking points were found to be higher when the fat was heated continuously and rapidly than when there was a gradual rise of 5°C . at intervals of 10 minutes, this being due to the slowness with which the reagent reacts. To obtain better results the temperature was held at each interval of 5°C . beginning at 150°C . for 10 minutes. The smoking temperature was then found to be much lower.

Kamm (1923) stated regarding the fuchsin bisulphite test:

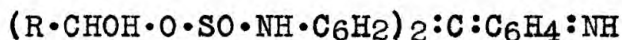
Aldehydes restore color to Fuchsin Aldehyde Reagent whereas ketones do not. The reagent is a dilute solution of rosaniline or fuchsin hydrochloride (magenta) that has been decolorized by sulfur dioxide.

Rosaniline HCl + 2 H₂SO₃
Crimson color



The aldehyde reverses this reaction due to a removal of H₂SO₃ from the methane carbon and a regeneration of the quinoid linkage. The restored color is not identical with the original fuchsin color but possesses a distinct bluish tinge. This is due to a reaction between the aldehyde and amino groups.

He considered that the recently proposed formula for the aldehyde-dye,



was still open to question. Kamm (1923) continued:

In general those reagents which remove sulfurous acid will restore the fuchsin color. This is true of organic amines, inorganic alkalis, and even of certain hydrolysable salts. Heating the reagent restores the color due to the dissociation of the fuchsin-sulfite compound. Although the restored color lacks the typical bluish tinge produced by aldehydes, it is always advisable to apply the test in the cold and to bear in mind the possible interferences.

Porter, Michaelis and Shay (1932) in a study of the behavior of edible fats and oils used as frying media found little apparent breaking down in the fats with heat alone under test conditions. There was a slight acid formation and an increase in viscosity and gum formations at higher temperatures. An objectionable flavor could be noticed when there was two per cent acid, expressed as oleic. The breaking down of a fat with the

formation of acid was a direct result of a reaction with water at elevated temperatures. These workers found that in both the experimental and bakery data up to 0.75 per cent acid the rate of acid formation was comparatively small. Beyond that point, the rate was considerably greater, probably because the acid acted as a catalyst to speed the reaction.

Lowe, Nelson and Buchanan (1940) reported experiments which had been started in 1933. These were primarily a study of lards, however, a few other fats were used such as corn oil and hydrogenated cottonseed oil. Tests were made on the fats when fresh and after the frying of potato chips and doughnuts for as long as 10 hours and 15 minutes. These workers found that gum formed at the edge of the container and the fat line during the heating period. The quantity was greater with the oils than with the fats. It was also reported that all fats darkened in color with use, the fats that smoked early in the cooking procedure darkening more than the fats with a higher smoking temperature. Some of the lards had a disagreeable and objectionable odor when first heated. Usually the odor of the lards decreased as the heating continued until a point was reached at which the odor of breaking down or burning fat became evident. The higher the temperature at which the fat was used the more rapid and greater was the breakdown of the fat. The smoking temperature was lowered during use, usually as the temperature of frying was increased. It was also found in this study that

in general the lard smoked more rapidly if the initial free fatty acid content was comparatively high. This was not always consistent. A greater amount of free fatty acid was present in fats heated to higher temperatures. As in previous studies, these workers found a negative correlation between the smoking point and the free fatty acid content.

There tends to be a wide variation in the literature regarding the highest percentage of fatty acids a fat may contain before an unpleasant flavor is imparted to the food. Thiessen (1939), after frying food for 18 hours, found the highest percentage of fatty acid present to be 0.755. The acid increase with 12 hours of frying was not sufficient to cause a disagreeable flavor in the doughnuts. The highest percentage of free fatty acids in this group was 0.677. The flavor of the doughnuts fried in fat heated for 18 hours was inferior to that of doughnuts fried in fat heated for a shorter time. It was not decided whether fats after heating 12 to 18 hours had deteriorated to the extent of being harmful for human consumption. The palatability committee of Thiessen's experiments apparently suffered no ill effects. Porter et al. (1932) in a study of the behavior of edible fats and oils when used as frying media have stated that an acid content above 2.0 per cent gives an objectionable flavor in the fried product. Lowe (1940) has found that in general the palatability scores were lower for doughnuts fried in a fat which had been used about eight hours than those fried in a fresh sample of the fat.

Morgan and Cozens (1919) found that heating fat alone for the same period as that used for cooking doughnuts did not result in as great changes in the fat as when food was actually cooked in it. They also found that the fats with the greatest amount of free fatty acids were absorbed more than those containing a lesser amount of free fatty acids.

A study of deep-fat frying at high altitudes was reported by Thiessen (1940). In this study it was found that fats could be used over and over for deep-fat frying if they were not heated to extremely high temperatures. Fats heated up to 12 hours did not affect the quality of flavor of the product cooked therein. Doughnuts and fritters were made with desirable flavors using lards, corn oil and a hydrogenated fat. A cheaper grade of lard was the only fat which resulted in a product undesirable in flavor. Oils were rated higher than the solid fats for frying potato chips. In this same study it was found that quality differences using various fats as frying media were more evident with potatoes than with dough mixtures. Thiessen found that off flavors in doughnuts fried in fat which had not been overheated and had been strained, cooled, covered closely and stored in a cold place were not evident until the fats had been used 12 hours or more.

In experiments on frying potato chips by King et al. (1936) several lards were used, also a hydrogenated lard, a hydrogenated cottonseed oil, a highly refined cottonseed oil and a highly

refined peanut oil. These workers found that the flavor of potato chips fried in peanut oil was placed above the flavor of those fried in the other fats. The results of the various fats used showed fat absorption to be about the same in the potato chips. After 10 fryings, none of the fats had a high free fatty acid content. The percentage of free fatty acids in the fat extracted from the potato chips was greater than in the frying fat. A comparison of the color of the different fats before the first and after the tenth frying showed greater discoloration in the lards, with the exception of the hydrogenated lard. The least deterioration as indicated by color was in the oils.

Lantz and Carlin (1938) stated that production of fried foods in very large quantities in commercial establishments is one of the severest tests for the edible fats on the market. The fats used in tests by these workers included three all-hydrogenated fats and two blended or compound shortenings. From 3,800 to 4,000 pounds of each fat were used in these experiments. For the frying of doughnuts, potato chips and fish, on a large scale, the fats were held at temperatures of $176.7^{\circ}\text{C}.$ to $204.4^{\circ}\text{C}.$, often for long periods of time. These workers found the increase in free fatty acids to be steady and rapid for the first 50 hours until a point of equilibrium was reached where the addition of fresh fat counterbalanced the rate of free acid formation. Again it was found that as the free fatty acid content increased the smoking point was lowered accordingly. The

broad conclusion made by these workers was that from the stability viewpoint, the decided advantages of certain types of fats when used for deep-fat frying is exaggerated.

Broeg (1940) found deep-fat frying to be an abused art in cookery. This was due to the lack of proper instruction from equipment manufacturers and from fat and oil manufacturers. He found that the instructions given the consumer were contradictory in that they stressed the importance of regulating the temperature yet in the tables containing the temperatures at which the foods were to be fried there was a range of as much as 35°C. to 50°C. for frying the same product. It is evident that all of the temperatures suggested could not be correct. Broeg recommended "shallow frying" rather than deep-fat frying; the use of a kettle which is not too large for the amount of food being fried; and the use of the smallest quantity of fat expedient for cooking the food. In selecting equipment Broeg stated, "-----have the greatest single layer frying surface area to a minimum amount of fat and sufficient B.t.u. input to maintain correct temperatures."

RESULTS AND DISCUSSION

The smoking points of 27 different fats and oils were determined. Using a four and one-half inch silica evaporating dish with the visual method, these smoking temperatures showed a range from a high of 245°C . to a low of 170°C . (Table 1).

Swift's Bland Lard with a smoking point of 234°C . had the highest smoking point of the animal fats used. The decomposition point of the other lards ranged from a high of 227°C . to a low of 174°C . Advance and Vegetole are combinations of vegetable and animal fats. The Vegetole had the lowest smoking point of any of the fats studied.

When a six-inch frying pan was used for heating the fat and oil samples the smoking points of all the samples were from two to four degrees lower than when the four and one-half inch silica evaporating dish was used. This resulted in an average drop in the decomposition point of 2.2°C . (Table 1).

The smoking points when obtained by the fuchsin bisulphite test for aldehydes gave still lower smoking points; they ranged from 20°C . to 40°C . and averaged 24.6°C . lower than those obtained when the visual method was used (Table 1).

Table 1. Smoking points using different methods of determination.

Name of Fat	Evaporating Dish 4½ in.	Frying Pan: 6 in.	Fuchsin Bisulphite
	°C.	°C.	°C.
Vegetable fats and oils:			
Soybean Oil	245	243	---*
Primex B and C	242	240	205
Snowdrift	237	236	210
Primex	237	236	200
Wesson Oil	237	235	205
Puritan Oil	236	235	210
Spry	236	234	203
Mazola Oil	233	230	205
Penick Oil	232	230	205
M. F. B.	230	228	205
Covo	229	227	208
Dexo	229	226	208
Kneedit	228	225	200
Flakewhite	208	205	185
Peanut Oil	199	197	178
Cocoanut Oil	195	193	---*
Crisco	190	187	180
Animal fats:			
Swift's Bland Lard	234	230	205
Clix	227	224	200
Armour's Leaf Lard	205	203	188
Homemade lard	198	197	180
Wilson's Lard	189	188	165
Armour's Star Lard	185	183	165
Sunnyfield Lard	180	179	163
Rex Lard	174	173	155
Combination vegetable and animal fats:			
Advance	209	207	183
Vegetole	170	168	150

*Omitted because of lack of sample.

The percentage of free fatty acids, as oleic, were determined by the standard method, as described by Morrow and Sandstrom (1927). These percentages are recorded (Table 2) for fresh fat and for fat after heating 2, 6, 12 and 20 hours. Also shown in this table are the smoking points of the fats and oils when heated in the four and one-half inch silica evaporating dish.

Table 2. Smoking point and percentage of free fatty acids, as oleic.

Name of Fat	Smoking:	Before	After Heating			
	Point	Heating	2 Hours	6 Hours	12 Hours	20 Hours
Vegetable fats and oils:	°C.	Per cent	Per cent	Per cent	Per cent	Per cent
Soybean Oil	245	0.014	0.028	0.055	0.065	0.114
Primex B and C	242	0.059	0.071	0.090	0.101	0.240
Snowdrift	237	0.009	0.042	0.108	0.116	0.152
Primex	237	0.061	0.084	0.106	0.124	0.251
Wesson Oil	237	0.028	0.029	0.109	0.165	0.199
Puritan Oil	236	0.014	0.014	0.053	0.083	0.160
Spry	236	0.029	0.031	0.053	0.086	0.232
Mazola Oil	233	0.113	0.140	0.159	0.170	0.376
Penick Oil	232	0.115	0.142	0.171	0.194	0.382
M. F. B.	230	0.009	0.027	0.086	0.144	0.183
Covo	229	0.057	0.072	0.085	0.114	0.145
Dexo	229	0.015	0.031	0.072	0.146	0.224
Kneedit	228	0.028	0.056	0.086	0.116	0.229
Flakewhite	208	0.085	0.109	0.131	0.185	0.244
Peanut Oil	199	0.244	0.276	0.278	0.373	0.411
Cocoanut Oil	195	0.013	0.120	-----*	0.596	1.018
Crisco	190	0.069	0.087	0.141	0.187	0.275
Animal fats:						
Swift's Bland Lard	234	0.015	0.043	0.069	0.145	0.205
Clix	227	0.030	0.041	0.058	0.115	0.243
Armour's Leaf Lard	205	0.130	0.141	0.214	0.323	0.404
Homemade lard	198	0.164	0.194	0.256	0.352	0.429
Wilson's Lard	189	0.244	0.261	0.265	0.310	0.432
Armour's Star Lard	185	0.310	0.426	0.435	0.480	0.565
Sunnyfield Lard	180	0.275	0.440	0.486	0.565	0.601
Rex Lard	174	0.416	0.440	0.471	0.533	0.565
Combination vegetable and animal fats:						
Advance	209	0.231	0.237	0.269	0.294	0.354
Vegetole	170	0.270	0.310	0.420	0.464	0.519

*Omitted because of lack of sample.

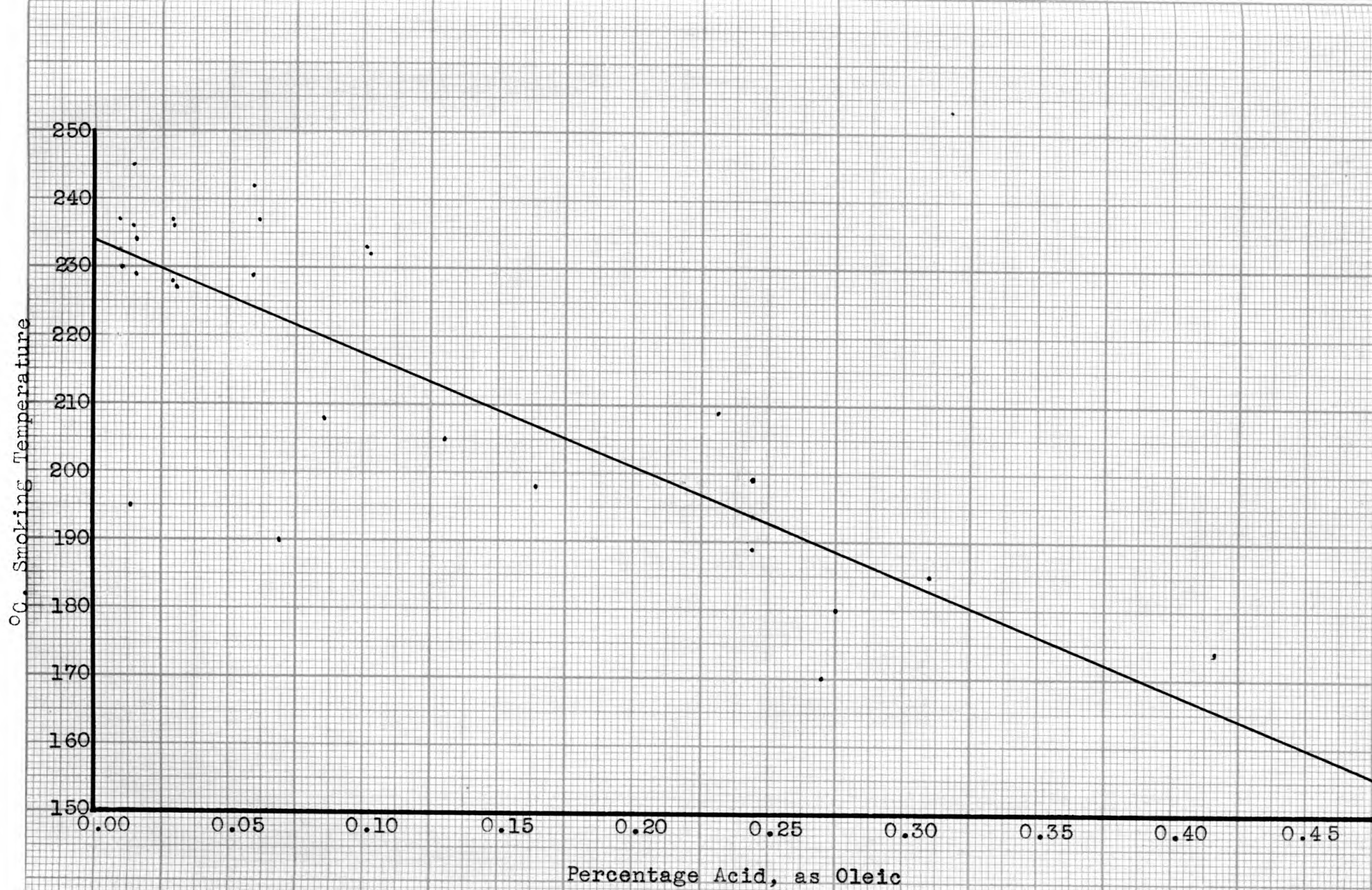


Fig. 1. Relation of smoking temperature to acid number.

The smoking points obtained in the present study are for the most part similar to those published by Blunt and Feeney (1915). The table showing the smoking temperatures of fats and oils and free fatty acid, as oleic, published by these workers includes 12 fats and oils and is the one quoted in literature most frequently today. The range of smoking points in the study by Blunt and Feeney is from a high of 233°C. to a low of 136°C. (Table 3). In the present study the smoking points of comparable fats and oils range from a high of 237°C. to a low of 195°C.

Table 3. Comparison between results of Blunt and Feeney and those of the present study.

Name of Fat	:Previous:		: Previous :	
	: Study :	: Present :	: Study :	: Present :
	: Smoking:	: Study :	: Free :	: Study :
	: Points :		: Acid :	
	: °C. :	: °C. :	: Per cent :	: Per cent :
Cottonseed Oil (Wesson)	: 233 :	: 237 :	: 0.07 :	: 0.028 :
Snowdrift	: 232 :	: 237 :	: 0.06 :	: 0.009 :
Crisco	: 231 :	: 190 :	: 0.13 :	: 0.069 :
Leaf Lard	: 221 :	: 205 :	: 0.15 :	: 0.130 :
Butterfat	: 208 :	: ---* :	: 0.28 :	: ---* :
Leaf Lard-heated 5 hours	: 207 :	: ---* :	: 0.34 :	: ---* :
Bulk lard	: 194 :	: ---* :	: 0.51 :	: ---* :
A much used lard	: 190 :	: ---* :	: 0.61 :	: ---* :
Olive Oil	: 175 :	: ---* :	: 0.92 :	: ---* :
Peanut Oil I	: 162 :	: 199 :	: 1.10 :	: 0.244 :
Peanut Oil II	: 149 :	: ---* :	: 1.64 :	: ---* :
Cocoanut Oil	: 136 :	: 195 :	: 1.90 :	: 0.014 :

*Comparable fats not included in present study.

The decomposition points of fats and oils found by different workers are somewhat dependent upon the exact method used. However, the free acid, as oleic acid, is determined by a standard method and should not vary greatly due to technique. A comparison of the results of Blunt and Feeney with those obtained in the present study (Table 3) indicated that the greatest improvement in the manufacturing process of the fats was from the standpoint of acid number. Of the six fats compared, the acid number was much lower in the present study for all of the fats, with the exception of the leaf lard. The latter was only slightly lower. Improved methods of manufacture may account for the lower percentage of free acid, as oleic, in the six fats. Crisco, the fat which also showed a decrease in the smoking point has been recently altered by the manufacturers to improve its creaming and shortening characteristics. This alteration has resulted in vapor being given off at a temperature somewhat below the smoking point of most other vegetable oils and hydrogenated fats.

The new Swift's Silverleaf Bland Lard resembles a hydrogenated fat although it contains only a small percentage of hydrogenated lard. A small amount of gum guaiac, up to one-tenth of one per cent, has also been added to this fat to protect it against rancidity.

Vegetole is a mixture of animal and vegetable fats which is "texturated." This process results in a product which

resembles hydrogenated fats in that it has a white color and is of a creamy consistency.

In the present study when a six-inch frying pan was used as the container in which fat samples were heated, the decomposition temperatures were slightly lower than when the four and one-half inch evaporating dish was used. This was undoubtedly due to the increase in surface area. It has been shown by several workers that the greater the surface area, the lower the smoking point.

The results of the present study are also comparable with those of Sprague (1919) who made a similar study of six fats, using the visual and chemical methods (Table 4).

Table 4. Comparison of results of Sprague and those of the present study using similar methods to determine the smoking point.

Name of Fat	Sprague		Present		Sprague		Present		Sprague		Present	
	3½ in.		4½ in.		6 in.		6 in.		Test 3½ in.		Test 4½ in.	
	Evaporating		Evaporating		Frying		Frying		Evaporating		Evaporating	
	Dish		Dish		Pan		Pan		Dish		Dish	
	°C.		°C.		°C.		°C.		°C.		°C.	
Wesson Oil	235		237		222		235		207.5		205	
Mazola	230		233		218		230		202.5		205	
Olive Oil	178		---	*	167		---	*	167.5		---	*
Crisco	231		190		219		187		202.5		180	
Lard Compound	226		---	*	214		---	*	197.5		---	*
Leaf Lard	221		205		210		203		192.5		188	

*Comparable fats not included in this study.

It was found in the chemical method used by Sprague that the rise in temperature of the heating fat had to be controlled to a rise of $5^{\circ}\text{C}.$ at intervals of 10 minutes. If the rise in temperature of the heating fat was continuous, the results were $20^{\circ}\text{C}.$ to $30^{\circ}\text{C}.$ higher.

The results of the fuchsin bisulphite tests were obtained with difficulty. Care had to be exerted to keep the solution cold, as ordinary temperatures may cause the solution to change color. When attempts were first made to determine the decomposition point of fats, the fuchsin bisulphite often changed color long before the decomposition temperature was reached. After considerable preliminary work it was found that in order to obtain consistent results it was important —

- (a) to have all equipment carefully cleaned;
- (b) to connect apparatus when fat sample was heated to within $100^{\circ}\text{C}.$ of the smoking point;
- (c) to keep U-tube immersed in ice water;
- (d) to regulate rate at which fumes were drawn through apparatus; and
- (e) to regulate rate of temperature rise of the fat sample since the reagent requires two to five minutes to react.

The fuchsin bisulphite tests resulted in smoking temperatures much lower than those obtained when the visual method was used. This was probably due to the ability of the chemical compound to react with quantities of acrolein too small to be

detected with the naked eye. Although these results are not the true smoking point, as usually defined, they do represent the temperature at which volatile material begins to evolve from the sample. A comparison was made between the smoking points when the visual method and when the chemical method was used. The differences were as much as 37°C. in the Primex B and C and a little as 10°C. in the Crisco. It is probable that the recent changes in the process of manufacturing Crisco so the product has greater creaming qualities is responsible for the small difference in the visual and chemical smoking point tests as compared with other fats.

In the present study the lards had a much higher initial free fatty acid content than any other fat used. The corn oils, Mazola and Penick, had a higher free fatty acid content than the other vegetable fats and oils.

A comparison of the increase in fatty acids, as oleic, expressed both in acid number and percentage are shown in Table 5. There was no consistent increase in the figures of these fats and oils.

Table 5. Comparison of increase in fatty acids, as oleic, expressed in grams and percentage.

Name of Fat	Grams Oleic Acid Before Heating	Grams Oleic Acid After 20 Hours Heating	Increase Expressed as Grams Oleic Acid After 20 Hours Heating	Increase Expressed as Percentage After 20 Hours Heating
Vegetable fats and oils:	Acid number	Acid number	Acid number	Per cent
Soybean Oil	0.028	0.228	0.200	717
Primex B and C	0.117	0.476	0.359	307
Snowdrift	0.019	0.302	0.283	1515
Primex	0.121	0.499	0.378	314
Wesson Oil	0.056	0.396	0.340	608
Puritan Oil	0.028	0.318	0.290	1042
Spry	0.058	0.461	0.403	696
Mazola Oil	0.225	0.748	0.523	232
Penick Oil	0.229	0.760	0.531	232
M. F. B.	0.018	0.364	0.346	1952
Covo	0.112	0.288	0.176	156
Dexo	0.030	0.445	0.415	1371
Kneedit	0.055	0.455	0.400	730
Flakewhite	0.170	0.486	0.316	185
Peanut Oil	0.486	0.818	0.332	68
Cocoanut Oil	0.026	2.026	2.000	7791
Crisco	0.136	0.547	0.411	301
Animal fats:				
Swift's Bland Lard	0.029	0.407	0.378	1301
Clix	0.060	0.484	0.424	711
Armour's Leaf Lard	0.259	0.803	0.544	210
Homemade lard	0.327	0.854	0.527	160
Wilson's Lard	0.486	0.859	0.373	76
Armour's Star Lard	0.616	1.124	0.508	82
Sunnyfield Lard	0.547	1.195	0.648	118
Rex Lard	0.537	1.123	0.586	35
Combination vegetable and animal fats				
Advance	0.459	0.705	0.246	53
Vegetole	0.537	1.033	0.496	92

It is evident that a table showing only the increase of fatty acids expressed in percentage increase (Table 5) would be misleading as some of the fats which increased only slightly during the 20-hour heating period, actually showed a high percentage increase. For example, the free acid, as oleic, in Snowdrift increased 0.283 grams during the 20-hour heating period. However, the percentage increase was 1515 per cent which was much greater than many other fats that had a higher initial free fatty acid content. M. F. B. and Peanut Oil vary only slightly in the increase expressed as acid number, these numbers being 0.346 and 0.332 respectively. There was a great difference between the two when the increase was expressed as percentage. The M. F. B. had a percentage increase of 1952, the Peanut Oil had an increase of only 68 per cent. Swift's Bland Lard acid number increase was 0.378. This figure was considerably lower than the other lards with the exception of Wilson's Lard. However, the percentage increase of the Swift's Bland Lard was 1301, this figure was a great deal above the percentage increases of the other lards used in this study. There was a wide variation in the results of the fatty acid content expressed both in grams and percentage, probably due to the composition of the fat.

The odors of these fats and oils while being heated varied greatly, ranging from those with practically no odor to a characteristic odor in the Soybean Oil and in lards. Although all of the lards had characteristic odors they differed greatly in intensity. The Swift's Bland Lard after being heated had the

definite odor of lard, although not as strong as some of the other lards. Lowe in a recent study stated that the odor of commercially rendered lards varied greatly. Different methods of rendering tended to produce lards each with its own characteristic odor. It has also been found by other workers that lard odors are volatile and tend to decrease during use. Corn oils had a definite odor of corn which was not objectionable. There was practically no odor present in many of the fats such as the hydrogenated fats and oils.

Soybean Oil had a definite objectionable "fishy" odor which may be due to the degree of refining. Soybean products may gradually be introduced with increasing favor in North America, but prejudice and custom must first be overcome. Until recent years the quantity of Soybean Oil produced was quite small and was used chiefly in the manufacture of paints. The refining process has not yet been perfected, in all instances, to the point of completely overcoming rancidity. Soybean Oil may be used for deep-fat or shallow frying or as a salad oil.

The colors of the melted fats and oils were noted after 20 hours of heating. The colors ranged from a light yellow to a dark brown color with a greenish cast. The fats that turned to a light yellow color were Covo, Spry, Clix, Dexo, Crisco and Coconut Oil. These appear in order of intensity although in this group there was little difference noticeable. The following group also had a yellow color although it was darker. In order these were Primex B and C, Wesson Oil, M. F. B., Primex and

Snowdrift. There was a change from the original color in the next group to a light brownish yellow. Included in this group were Flakewhite, Wilson's Lard, Soybean Oil, Swift's Bland Lard, Kneedit and Fluffo. Those fats having a golden brown color after 20 hours of heating were Advance, Peanut Oil, Armour's Star, Puritan Oil and Mazola. A reddish brown color, considerably darker than the group preceding was found in Sunnyfield Lard, Rex Lard and Vegetole. The Armour's 100 per cent Pure Leaf Lard and the homemade lard turned to a brown color with a greenish cast. These color changes in the last two fats were evident after two hours of heating.

In the present study there was no apparent correlation in the color of the fat after 20 hours of heating and the smoking point. This may be due in part, at least, to the fact that food was not actually fried in this series of experiments. In other experiments in which food has been cooked it has been reported that the darkening in color was due to the breaking down of the fat and the accumulation of brown fat particles. When there was a large amount of these browned particles the appearance of the product being cooked was speckled. Under otherwise identical conditions this mottled appearance occurred to a greater extent in fats that smoked earlier in the frying process.

There were slight settlings in the following fats when they were heated: Puritan Oil, Cocoanut Oil, Soybean Oil, Peanut Oil, Wesson Oil, Covo, Spry and Advance. This was probably due to the composition of the fat and to the method of manufacturing. Heavy

settlings were evident in the homemade lard.

All fats produced a gum formation at the top rim of the fat surface, close to the sides of the container, after being heated for 12 hours or longer. There was also a noticeable increase in viscosity.

Lowe and others in a recent study found that lards with mild odors were preferred by the consumer. These workers also found that a high rather than a low smoking point was desirable, at least 190°C. or higher. In the same study it was suggested that the free fatty acid content be below 0.30 per cent, as oleic acid, for better grades of lard.

The homemade lard used in this study had the most unpleasant and the strongest odor of any of the fats used. Strong flavors would no doubt have been imparted to foods fried in this medium. The smoking temperature of the homemade lard was 198°C., only slightly above the temperature 190°C. recommended as the lowest smoking temperature desirable for fats used for deep-fat frying.

The fats and oils used in this study differ in the size of containers in which they are distributed. Some are marketed in small quantities for use by the housewife and some in 50-pound, 100-pound and 400-pound drums for use in institutions.

Soybean Oil is shipped mostly in tank cars to the large manufacturers of mayonnaise and salad dressings and for other uses, although it is sold in five-gallon cans.

Primex B and C is a hydrogenated fat which is especially suited for deep-fat frying, as stated by the manufacturers, and

is packed in large drums for institutional use. Primex, a similar product is also sold to restaurants.

Cocoanut Oil is used largely in the manufacture of candy and by bakers.

Puritan Oil is packed in five-gallon cans. This product is the same as Fluffo, which is packed in one-gallon cans. Oils may be distributed in 400-pound steel drums.

Covo and Spry are manufactured by the same company. Spry is sold in one-pound and three-pound containers. Covo is packed in one- and three-pound containers and also in larger containers for institutional trade and is manufactured to be slightly firmer than Spry to meet the demands of the trade which uses mechanical mixing methods.

Heavy duty M. F. B. is made for institutional use.

Advance, Vegetole, Wesson Oil, Mazola, Penick Oil and Peanut Oil are packed in both small containers and in large containers. Armour's Leaf Lard, Wilson's Lard, Armour's Star, Rex Lard, Sunnyfield, Dexo, Kneedit, Flakewhite, Crisco, Swift's Bland Lard, Clix and Snowdrift are usually purchased in household-size containers.

All of the prices of the various fats were not available so a detailed study of these was not made. Of the prices obtained both of the household-size package and of the institutional size drums, the range was from six to thirteen cents per pound. Many factors are involved in the prices of fats and oils such as availability, size of package or container, advertising,

present market conditions, and the retail or wholesale grocer from whom the product is purchased.

SUMMARY

1. The smoking temperatures found in this study determined by the visual method, using a four and one-half inch silica evaporating dish, ranged from a high of $245^{\circ}\text{C}.$ to a low of $190^{\circ}\text{C}.$ for the 17 vegetable fats and oils. The eight animal fats studied ranged from $234^{\circ}\text{C}.$ to $174^{\circ}\text{C}.$ The combination vegetable and animal fats, of which there were two, showed decomposition points of $209^{\circ}\text{C}.$ and $170^{\circ}\text{C}.$

2. There was an average drop of $2.2^{\circ}\text{C}.$ in the decomposition points when using a six-inch frying pan as compared with the evaporating dish.

3. The fuchsin bisulphite test for aldehydes resulted in still lower smoking points, averaging $24.6^{\circ}\text{C}.$ lower than those obtained when the visual method was used.

4. The smoking temperatures of the samples of fat used in the present study were somewhat higher than those of comparable fats used in other studies. This was probably due to the method used, individual technique, and improved methods of manufacturing the fats and oils.

5. The percentages of free fatty acids before and after heating were:

	Before heating			After heating 20 hours	
		Range			Range
Animal fats	0.009	to 0.244	:	0.205	to 0.601
Vegetable fats	0.015	to 0.416	:	0.114	to 1.018
Combination			:		
vegetable and			:		
animal fats	0.231	to 0.270	:	0.354	to 0.519

6. The percentages of free fatty acids, as oleic, in fats tended to be inversely proportional to the smoking point.

7. There was no apparent relationship between the color of the fat after 20 hours of heating and the smoking point.

8. The odors of the heating fats varied from those with practically no odor to a characteristic odor in the soybean oil and lards.

9. All fats produced a gum formation after being heated 12 hours or more. There was a noticeable increase in viscosity.

10. Most of the fats used in the present study would be suitable as a frying medium if the temperature were carefully regulated.

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